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Collisional Relaxation of Vibrational Energy Transients
in the Methylcyclopropane System.

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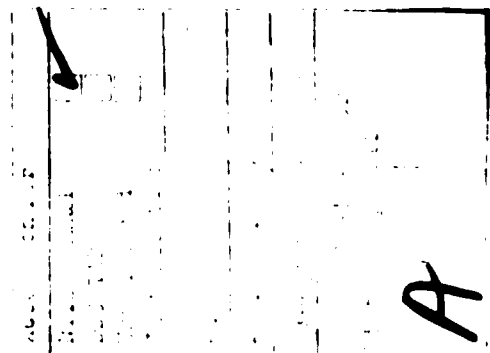
Collisional Relaxation of Vibrational Energy Transients in the
Methylcyclopropane System. A Variable Encounter Method Study.*

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Abstract

The Variable Encounter Method has been used to study vibrational energy transients in the isomerization of methylcyclopropane to various butenes. This system was studied with reactor surface temperatures of 800 K to 1130 K and average numbers of collisions per encounter with the reactor of 5.6 and 20.0. The reaction rate was treated on the basis of total, rather than individual butene rates, because of butene product interconversion. An exponential model of energy transfer was found to give the best fit to the data with the average down step energy $\langle \Delta E' \rangle$ decreasing from 1860 cm^{-1} to 1415 cm^{-1} with increase of temperature over the range studied. Incubation times increased from 14 to 19 collisions with increase in temperature, and these times, together with values of the conventional relative collision efficiency β and values of $\langle \Delta E' \rangle$, are compared with those of other molecules studied by VEM. The calculated transient population distributions and the associated sequential reaction probabilities are also displayed.



Introduction

The Variable Encounter Method¹⁻⁴ (VEM) provides a simple technique for the study of the transient region in vibrational energy transfer between gas molecules and a surface. In this technique, initially cold polyatomic molecules experience a known, and experimentally variable number of collisions with a hot surface. After each series of collisions (an encounter) with the surface, the molecules are reequilibrated to their initial low temperature before reentering the reactor. In principle, the reaction energy threshold constitutes an absorbing barrier. The level of vibrational excitation, and hence rate of transient relaxation, is deduced from the rate of unimolecular reaction. The theory of the technique is presented in detail in ref. 2.

Previous studies have shown that the characteristic time required for the transient to relax (the "incubation time") is somewhat greater for the pyrolysis of cyclobutane to ethylene³ than for the isomerization of cyclopropane to propene.^{2,4} This comparison is appropriate since both molecules have similar levels of the critical reaction thresholds (E_0), 59.3 and 63.6 kcal mole⁻¹, respectively. In both cases, the rate of relaxation decreases as the wall temperature is increased. We speculate that the higher vibrational heat capacity of cyclobutane may be responsible, at least in part, for this difference. The VEM study of methylcyclopropane to butene is reported here. This molecule was chosen since it has related molecular structure to its predecessors, and similar reaction threshold, but has some lower vibrational frequencies and somewhat higher vibrational heat capacity than cyclobutane.

Experimental

The apparatus used in this study was similar to that of previous VEM studies. The reactor vessel consisted of a four-liter quartz flask with two attached cylindrical reactor fingers. Each reactor finger could be heated independently and had inside diameters of 4.2 cm and respective lengths of 5.9 cm and 21.0 cm (including the hemisphere which terminates the cylinder) giving average numbers of collisions per encounter, m , of 5.6 and 20.0. Temperature measurements were made with several chromel-alumel thermocouples cemented to the outside of the reactor. Typical reactor temperatures varied from 800 K to 1130 K, while flask temperatures varied from 350 K to 400 K.

Separation of the reaction products was performed by gas chromatography on a dual, column arrangement. The first column was 30' x 1/8" and consisted of ethylene glycol saturated with silver nitrate, 25% on 60-80 mesh chromosorb P. This was followed by a 4' x 3/16" 30% squalane on chromosorb P column. Both columns were maintained at 0°C. Complete separation of all products was obtained. Detection was performed by either FID or, at lower reaction percentages, by an 11.7 e.v. PID, with an increase in sensitivity.

The reactant methylcyclopropane was purified by gas chromatography on a preparative silver nitrate-ethylene glycol column, followed by fractional distillation at -78°C. A purity of 99.99% was obtained.

Prior to a run, the system was pumped down to $< 10^{-6}$ torr and reactant was introduced at a pressure of $1-2 \times 10^{-4}$ torr. Reaction times varied from several minutes to several hours with the amount of reaction being 1-80%.

Each reactor was aged before kinetic measurements were performed simply by pyrolyzing methylcyclopropane at 1 mtorr and 850°C. Some ethylene and a slight amount of propene production occurred in early work, but after several days, these dropped below 1% of the total products. A few percent of 1,3-butadiene which declined, but did not disappear with aging, was also present.

Results and Discussion

The isomerization of methylcyclopropane to butenes was investigated over the temperature range 800 K to 1130 K. Interconversion of the product butenes complicated a multichannel analysis of the data; hence, the reaction was treated on the basis of the total rate. Although early thermal studies report this reaction to be free of surface catalytic effects,^{5,6} the formation of ethylene and 1,3-butadiene (see above) indicates a very minor amount of side reaction.

The average probability of reaction per collision, $\bar{P}_c(m)$, was calculated from the apparent first order rate constant using simple kinetic theory of gases and the known reactor dimensions. Experimental values of $\bar{P}_c(m)$ versus temperature for the two reactors are shown in Fig. 1.

The distribution function for numbers of collisions in each reactor was determined by a Monte Carlo calculation of a large number ($5 - 20 \times 10^3$) of individual molecular trajectories. This distribution was then used in a simulation of the encounter process. In this iterative calculation, the entering molecule is represented by a normalized Boltzmann vector, \underline{N} , characteristic of the low temperature. Collision is then simulated by multiplication by a transition probability matrix. The resultant vector is then attenuated for loss due to escape and reaction. This cycle is repeated until $\underline{N} = 0$ or an extrapolation procedure may be employed. The details of these calculations are given in ref. 2.

An exponential distribution for the probability of a down transition ΔE upon collision was used: $P_{\Delta E} = A \exp(-\Delta E / \langle \Delta E \rangle)$ for $0 \leq \Delta E \leq 9000 \text{ cm}^{-1}$; $P_{\Delta E} = 0$, for $\Delta E > 9000 \text{ cm}^{-1}$. Here A is a normalization constant and $\langle \Delta E \rangle$ is an adjustable parameter taken to be independent of initial energy level (a "flat" model). Some calculations were also done with a gaussian probability distribution;

$P_{\Delta E} = A' \exp\{-(\Delta E - E_{mp})^2 / 2\sigma^2\}$, for $0 \leq \Delta E \leq 9000 \text{ cm}^{-1}$, and $P_{\Delta E} = 0$, for $\Delta E > 9000 \text{ cm}^{-1}$, here A' is a normalization constant, and E_{mp} and σ are adjustable parameters. The corresponding upsteps were determined by detailed balance and completeness.

The truncation at 9000 cm^{-1} is a practical computational feature to limit the transition probability matrix to more convenient dimensions. Due to this truncation, the effective average down transition size, $\langle \Delta E' \rangle$, is not equal to $\langle \Delta E \rangle$ except when the latter quantity is small.

The microscopic rate constants for reactant molecules excited to each energy level, which are required in the computer simulation, were calculated by RRKM theory. These calculations were grained commensurately with the graining of the transition probability matrix. Molecular and transition state vibrational frequencies, as well as critical threshold energy, E_0 , are required for this calculation. The molecular vibrational frequencies used here are those given Dorer⁷ and are listed in the Appendix. There is some uncertainty in the value of E_0 in this reaction. Chesick⁵ reported total high pressure Arrhenius parameters of $E_\infty = 65.0 \text{ kcal mole}^{-1}$ and $\log_{10} A_\infty (\text{s}^{-1}) = 15.45$. Using the set of activated complex frequencies given in the Appendix with RRKM theory, one calculates an E_0 of $62.3 \text{ kcal mole}^{-1}$. Setser⁶ reported Arrhenius parameters of $E_\infty = 63.2 \text{ kcal mole}^{-1}$ and $\log_{10} A (\text{s}^{-1}) = 14.8$, which gives a corresponding lower value for E_0 . Placzek⁸ reanalyzed the data of Chesick and concluded that the E_∞ value was about 1 kcal mole^{-1} higher than had been originally reported. Benson and O'Neal⁹ concluded that the E_∞ value was about $63.0 \text{ kcal mole}^{-1}$ on the basis of a biradical mechanism. We have adopted an E_0 value of $62.3 \text{ kcal mole}^{-1}$ and $\log A (\text{s}^{-1})$ of 15.5 with the transition state vibrational frequencies given in the Appendix.

Curves calculated on this basis with use of an exponential transition probability model are shown in Fig. 1. The corresponding values of $\langle \Delta E' \rangle$ (cm^{-1}) chosen to

fit the $m = 5.6$ curve are also shown. This choice is made because the calculated values of $\bar{P}_c(m)$ are more sensitive to the value of $\langle \Delta E' \rangle$ in the smaller m reactor. Lowering the assumed E_0 by one kcal mole⁻¹ (with the A_∞ factor held constant) would lower the values of $\langle \Delta E' \rangle$ required to fit the $m = 5.6$ reactor by about 100 cm⁻¹ and would lower the calculated $m = 20$ curve by approximately 25%. Raising the assumed E_0 has approximately the opposite effect. If the A_∞ factor is also adjusted to give the same high pressure rate constant, the effects of variation of E_0 are somewhat reduced. Gaussian models give higher $m = 20$ curves when fitted to the $m = 5.6$ data and do not fit the data as well as do exponential models. This was also found to be the case for the cyclobutane pyrolysis study (ref. 3). Values of $\langle \Delta E' \rangle$ calculated here are compared with those obtained in other VEM studies in Table I.

The fit to the $m = 20$ data is seen to be quite good at the higher temperatures, with some discrepancy at the lowest temperatures. This implies the presence of some surface catalytic process that is negligible at higher temperatures. Previous VEM studies of cyclopropane have also reported that possible surface effects⁴ (significantly smaller, however, than the discrepancy here) arise at lower temperatures, although any such complications were almost completely absent in the cyclobutane³ and cyclobutene¹⁰ study.

Transient population distributions were first calculated by Rubin and Shuler¹¹ and, for harmonic oscillator transition probabilities, were shown to relax through a series of Boltzmann distributions to the final temperature. In the iterative simulation here, transient distributions were also calculated and are shown in Figs. 2 and 3. It is evident that the intermediate distributions are not of Boltzmann type for the realistic transition probabilities employed here. The relaxation at low energy is much faster than that at higher energy; hence, the bulk "temperature" (as determined by the average energy) relaxes more quickly

than does the rate of reaction. This is particularly true at lower temperatures.

Values of the sequential reaction probabilities, $P(n)$ as a function of the number of collisions that the molecule has experienced up to that point, n , were also calculated by iterative simulation (Fig. 4). These plots that characterize the relaxation process depend somewhat on the reactor size, i.e., on the degree of falloff. It is seen that essentially no reaction takes place in the first few collisions, but relaxation is almost complete in about 30-40 collisions. Hence, especially in the $m = 5.6$ reactor, it is only those molecules that experience a number of collisions significantly greater than m that make a non-negligible contribution to the total amount of reaction. This is clearly seen in Fig. 5 where the total amount of reaction, $R(n)$, following the n th collision is plotted.

Incubation times as given by Dove and Troe¹² may be defined as

$$N(t) = N(0) \exp \left[-k(t - \tau_{inc}^{DT}) \right], \text{ as } t \rightarrow \infty$$

where $N(t)$ is the amount of reactant at time t and k is the steady state rate constant. Considering the relaxation to be a discrete rather than continuous process, it was shown that²

$$\tau_{inc}^{DT} = \lim_{j' \rightarrow \infty} \left[j' - \sum_{j=0}^{j'-1} P(j)/P(\infty) \right]$$

where $P(j)$ is the j th sequential reaction probability (Fig. 4). The reaction probabilities and, therefore, τ_{inc}^{DT} depend upon the degree of falloff, i.e., upon the fraction of molecules with energy greater than E_0 that react. Alternatively, the first mean passage time \bar{t}_{fp} as given by Kim¹³ and Widom,¹⁴ which is the average time required for a molecule to obtain an energy equal to or greater than E_0 , may be used to define an incubation time:

$$\tau_{inc} = \bar{t}_{fp} - \bar{t}_{fp}^{ss}$$

where \bar{t}_{fp} is a constant characteristic of the system and \bar{t}_{fp}^{ss} is the first mean passage time at the final temperature in the absence of any transient. The latter quantity and, therefore, τ_{inc} , depend only weakly (i.e., second order effects that become more pronounced at very high temperatures) on the degree of falloff; thus, τ_{inc} depends primarily only on the molecular characteristics (E_0 and densities of states), the transition probabilities and the initial distribution of the system. Both τ_{inc}^{DT} and τ_{inc} are characteristic times for the transient to relax and have been shown² to be equivalent in the limit of low pressure and low reaction probabilities. Values of τ_{inc}^{DT} and τ_{inc} for this and several other VEM systems studied to date are given in Table II. It is seen that the values of τ_{inc} are always lower than the corresponding values of τ_{inc}^{DT} due to the fact that the average energy and, therefore, the fraction of molecules over E_0 that react, increases as the transient relaxes. The approximate steady state fraction of molecules excited above E_0 that do not react prior to the next collision are (1100K): cyclopropane, 25%; cyclopropane-1,1-d₂, 30%; cyclobutane, 80%; methylcyclopropane, 90%. Of course, these values depend somewhat upon temperature. The values of τ_{inc} for the methylcyclopropane system are seen to be significantly higher than for cyclopropane or cyclobutane, and the same trend of increasing τ_{inc} with temperature is present.

The collisional efficiency may be defined as $\beta = P(\infty)/P(\text{strong collider})$ and have been calculated for an exponential model of the transition probabilities (Table III). These calculated values depend upon the transition probabilities model more so than do incubation times and are a more graphic measure of the efficiency of the gas-wall interaction.

Summary and Conclusions

A VEM study of the reaction of methylcyclopropane to butenes has been performed over the temperature range of 800 K to 1130 K. The reaction appears to proceed cleanly at the highest temperatures, but the presence of concomitant surface catalytic processes at the lowest temperatures is indicated by the poorer fit of the calculated curves, and the presence of small amounts of 1,3 butadiene, and trace ethylene side product. An exponential model for downstep probabilities gives a better fit to the data than does a gaussian model over the entire temperature range.

Comparison of this work with that on cyclopropane^{2,4} and cyclobutane³ indicates the following: i) $\langle \Delta E' \rangle$ decreases with a corresponding increase in τ_{inc} as the vibrational heat capacity of the molecule increases. ii) in all cases τ_{inc} is found to increase with increasing temperature. iii) exponential models provide better fit in cyclobutane and methylcyclopropane systems, whereas the best fit in the stronger-collision cyclopropane system is provided by either a gaussian or an intermediate-type (poisson) model. Optimally, small molecules in large reactors at higher temperatures are the preferred subjects and conditions for study. In most systems, especially methylcyclopropane, the most reliable data are also obtained at higher temperatures.

AppendixVibrational frequencies for RRKM calculations (cm^{-1})

Methylcyclopropane molecule:

3100, 3079, 3055, 3017(2), 2976(2), 2898, 1488, 1474, 1465, 1419,
1387, 1380, 1202, 1111, 1072, 1041, 1021, 1016, 983, 968, 911,
889, 810, 804, 756, 349, 291, 225

Activated complex:

3080, 3055, 3015(2), 2975(2), 2900, 1475, 1465, 1390, 1380, 1200(3),
1110, 1070, 1020, 1015, 980, 968, 910, 900, 810, 600, 500, 450,
350, 250, 150

Table I. Some values of $\langle \Delta E' \rangle$ (cm^{-1}) from VEM studies^a

<u>Molecule</u>	<u>Model</u> ^b	<u>Temperature, K</u>			<u>Reference</u>
		800	950	1100	
cyclopropane-d ₂	gauss.	3800	3100	2580	2
	expon.	~ 7000	2940	2280	
cyclopropane	gauss.	3500	2320	2040	4
cyclobutane	expon.	2190	1690	1480	3
methylcyclopropane	expon.	1860	1480	1415	this work

^a Some values by slight interpolation

^b Transition probability model given here is the one that fits the data better. Behavior is intermediate in the work of ref. 2 at higher temperatures, but $\langle \Delta E' \rangle$ becomes unrealistic at lower temperatures (more efficient energy transfer) on the basis of the exponential model.

Table II. Incubation times^a, τ_{inc}

<u>Molecule</u>	<u>Temperature (K)</u>		
	800	950	1100
cyclopropane	6.3	11.4	14.2
cyclopropane-1,1-d ₂	~ 4.5	9.8	12.8
cyclobutane	10.0	14.0	15.4
	(11.2) ^b	(16.0)	(18.1)
methylcyclopropane	13.6	19.1	19.3
	(15.1)	(21.7)	(22.8)

^a Expressed as number of collisions. Some values by slight interpolation or extrapolation.

^b Parenthetical quantities are τ_{inc}^{DT} values which are nearly identical to τ_{inc} for cyclopropane and cyclopropane-1,1-d₂.

Table III. Wall collisional efficiencies, β in the present system

<u>Temperature (K)</u>	<u>β</u>
800	0.48
950	0.33
1100	0.24

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Figure Captions

- Fig. 1 Plots of experimental values of $P_c(m)$ versus $T(K)$ for the two reactors: $m = 5.6$, ■ ; $m = 20.0$, ● . Also shown are solid curves calculated using an exponential transition probability model fitted to the $m = 5.6$ data at each of three values of T . The $\langle \Delta E' \rangle$ values given were then used to construct the calculated curve for $m = 20$.
- Fig. 2 Absolute population distributions $N(E)$ versus $E(\text{cm}^{-1})$ at 1100 K calculated for increasing numbers of consecutive collisions using an exponential transition probability model. The curves on the right represent magnification of the ordinate by a factor of 100. The $n = 39$ curve approximates the steady state distribution.
- Fig. 3 Relative population distributions, $N(E)/N(E)$ equilibrium, versus $E(\text{cm}^{-1})$ calculated for increasing numbers of consecutive collisions using an exponential transition probability model at (a) 800 K and (b) 1100 K. In both cases the distribution of the last collision shown approximates the steady state.
- Fig. 4 Histograms of calculated normalized sequential reaction probabilities $P(n)$ versus n , the number of consecutive collisions. Calculations were performed at 800 K and 1100 K using an exponential model of transition probabilities.
- Fig. 5 Calculated plots of the total amount of reaction following the n th collision, $R(n)$ versus n , the number of consecutive collisions. Calculations were performed at (a) 800 K and (b) 1100 K for both reactors using an exponential model of transition probabilities.

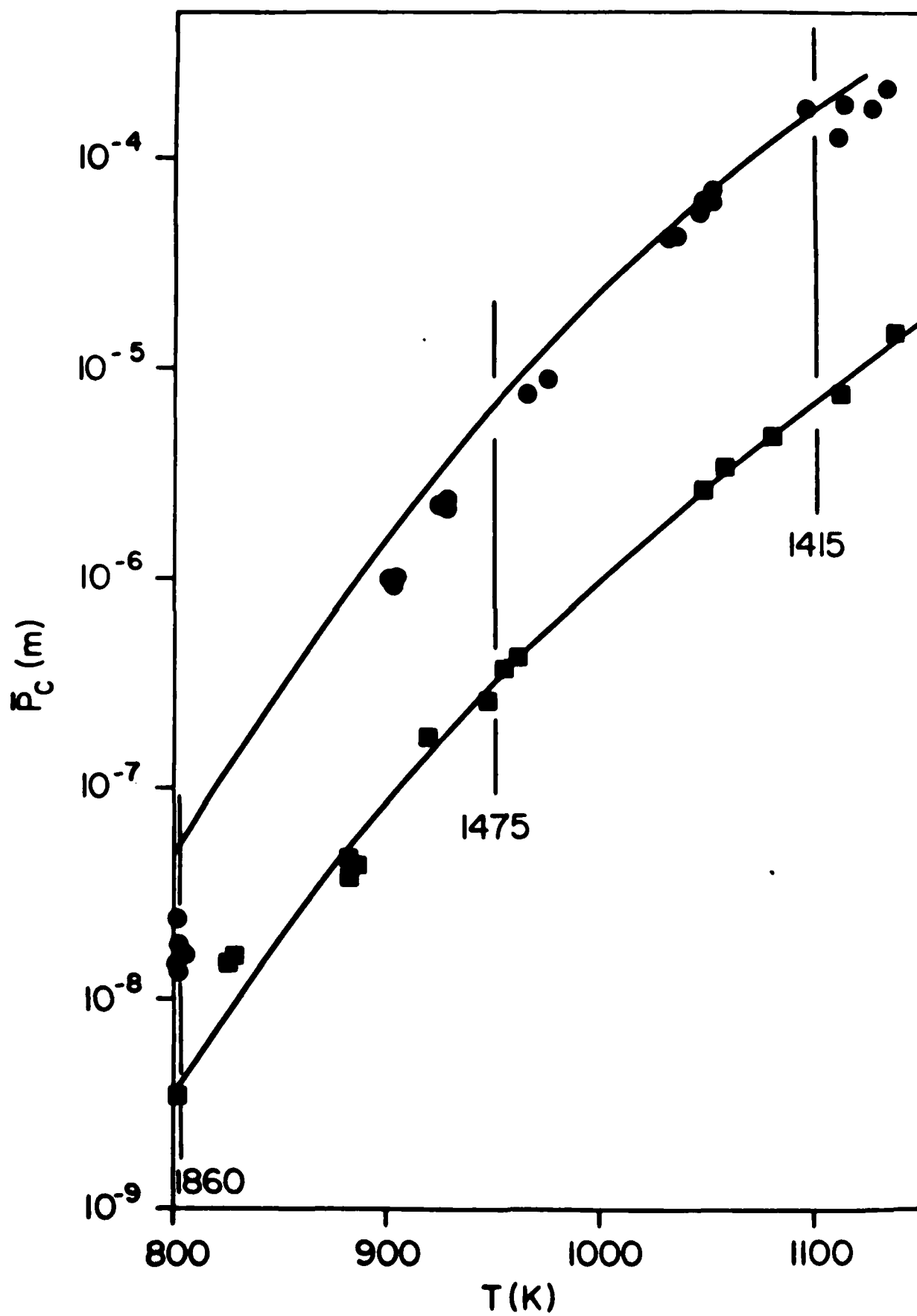
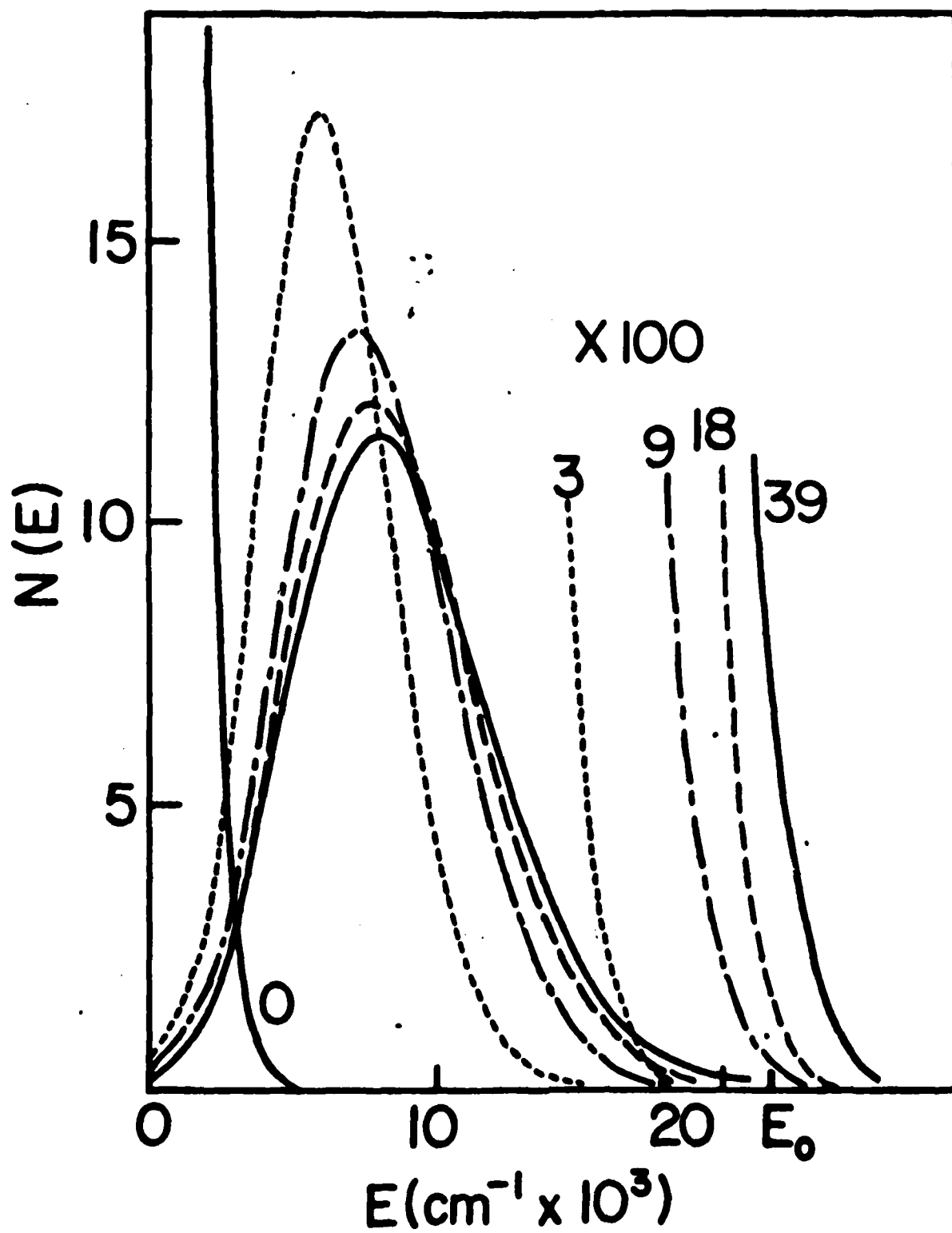


Fig. 1



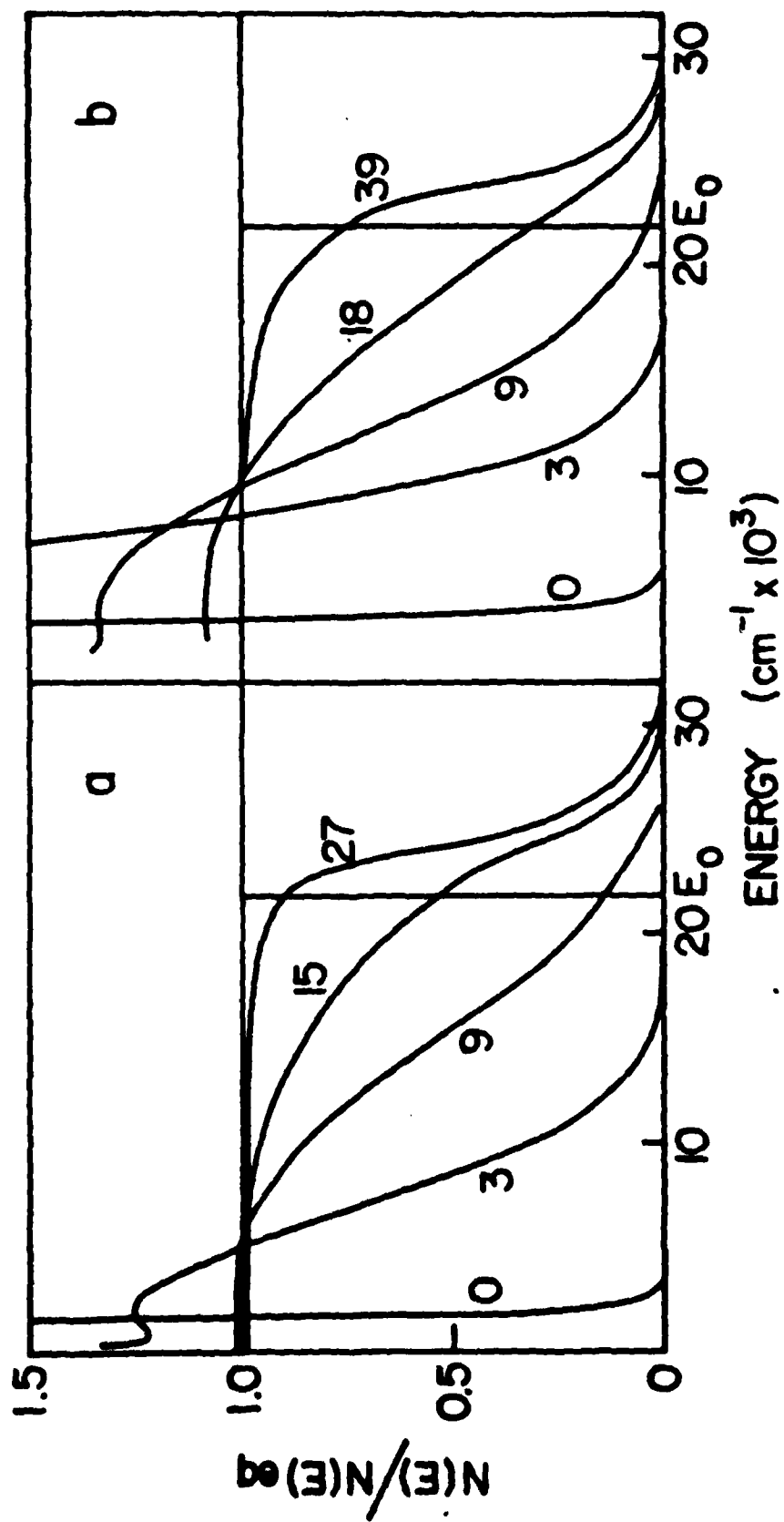


Fig. 3

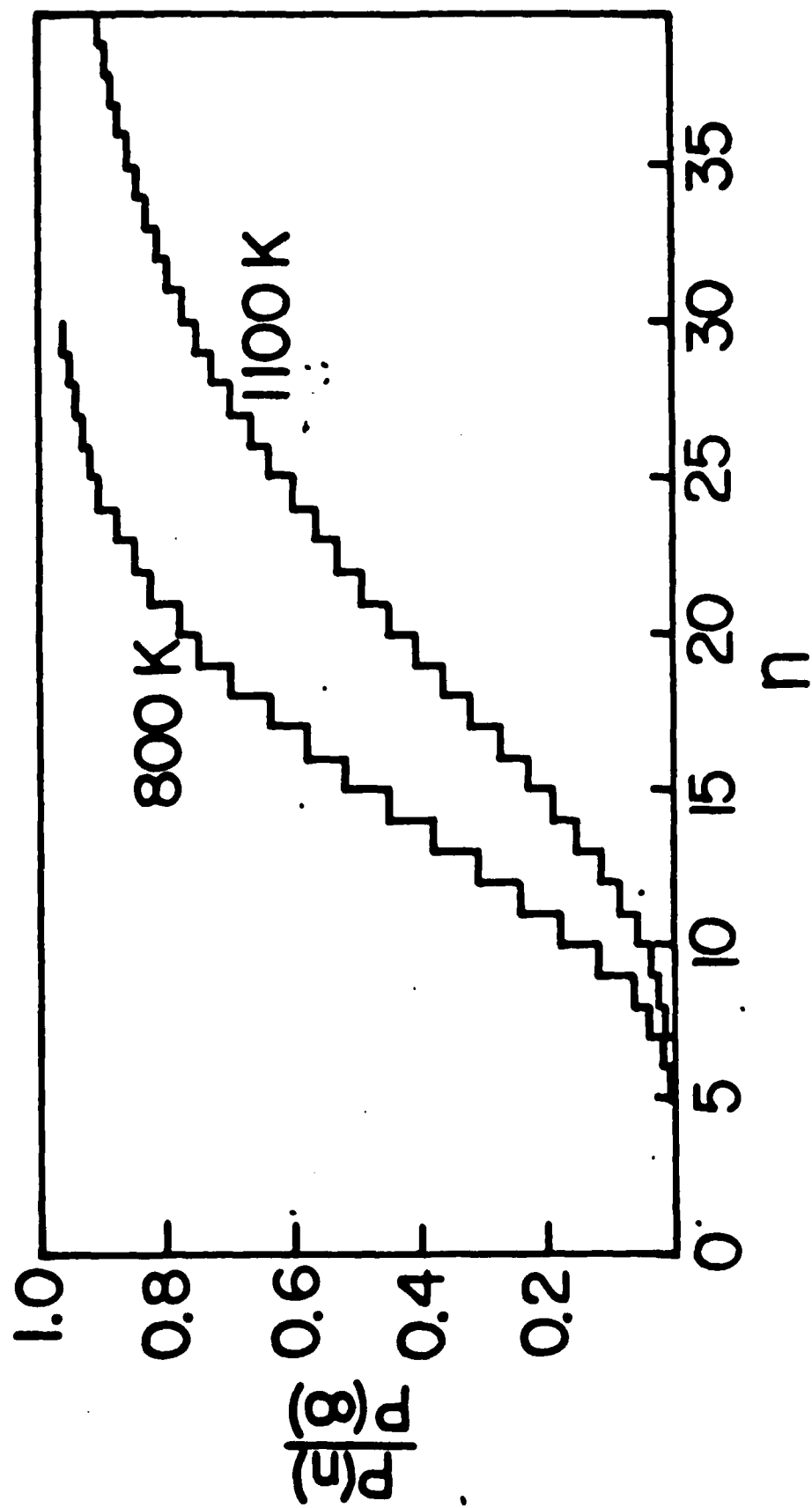
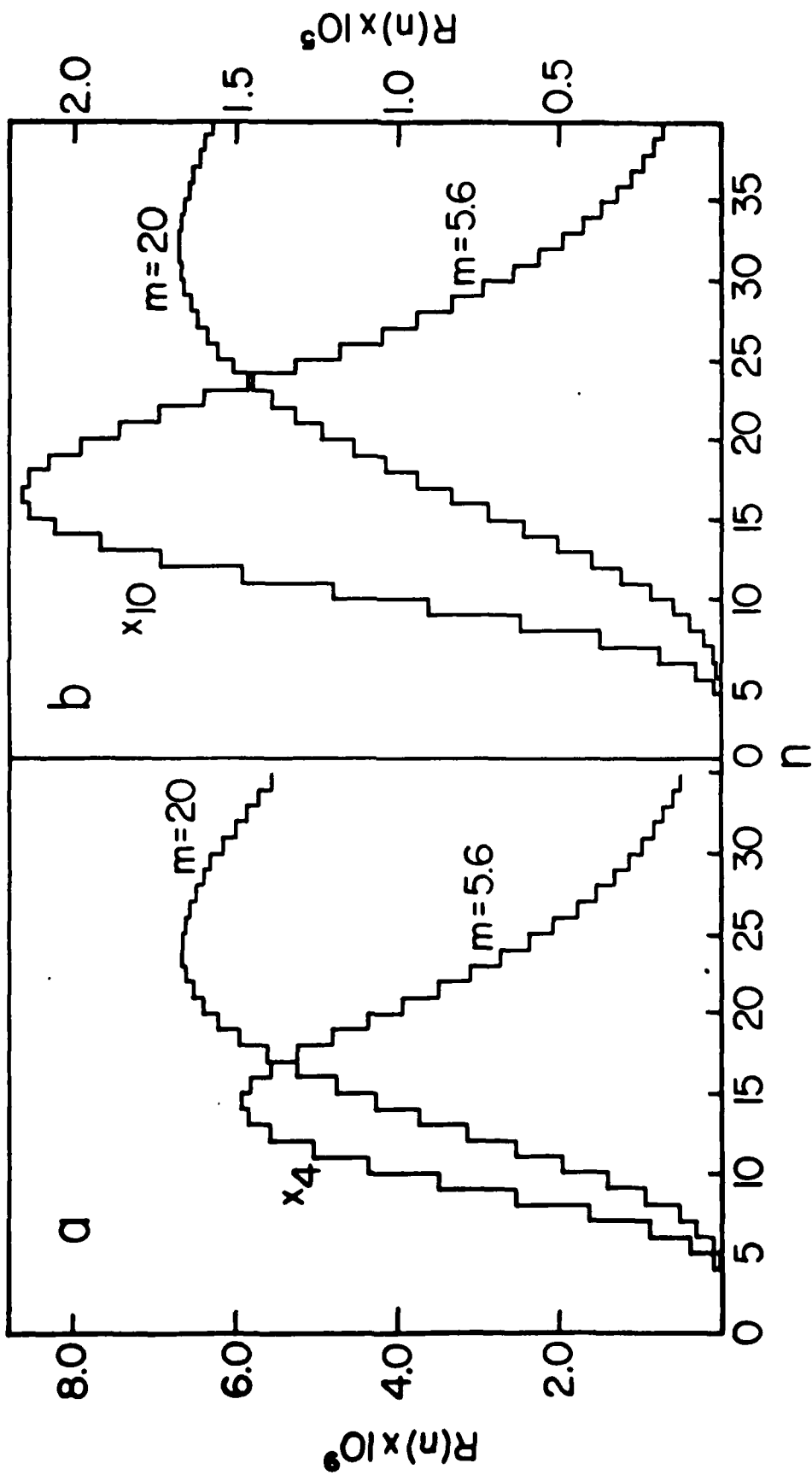


Fig 4



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